



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup> : <b>A44B 18/00</b></p>	<p><b>A1</b></p>	<p>(11) International Publication Number: <b>WO 99/40812</b></p> <p>(43) International Publication Date: 19 August 1999 (19.08.99)</p>
<p>(21) International Application Number: PCT/US99/02897</p> <p>(22) International Filing Date: 11 February 1999 (11.02.99)</p> <p>(30) Priority Data: 60/074,463 12 February 1998 (12.02.98) US</p> <p>(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 60/074,463 (CON) Filed on 12 February 1998 (12.02.98)</p> <p>(71) Applicant (for all designated States except US): BOARD OF TRUSTEES OPERATING MICHIGAN STATE UNIVERSITY - [US/US]; East Lansing, MI 48824 (US).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): TOMANEK, David [US/US]; 1136 Poplar Lane #4, East Lansing, MI 48823 (US). ENBODY, Richard [US/US]; 345 University Drive, East Lansing, MI 48823 (US). KWON, Young-Kyun [KR/US]; 1443D Spartan Village, East Lansing, MI 48823 (US).</p>		<p>(74) Agents: SIMINSKI, Robert, M. et al.; Harness, Dickey &amp; Pierce, P.L.C., P.O. Box 828, Bloomfield Hills, MI 48303 (US).</p> <p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p><b>Published</b> With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>
<p>(54) Title: MICRO-FASTENING SYSTEM AND METHOD OF MANUFACTURE</p> <p>(57) Abstract</p> <p>The present invention relates to a micro-fastening system and, more particularly, to a mechanical micro-fastening system employing a plurality of mating nanoscale fastening elements (16, 18) and a method of manufacturing a micro-fastening system in accordance with the teachings of the present invention. The mating nanoscale fastening elements (16, 18) are formed by functionalizing nanotubes having an ordered array of hexagons with pentagons and heptagons at particular heterojunctions.</p> <div data-bbox="738 1165 1291 1480"> </div>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## TITLE

### MICRO-FASTENING SYSTEM AND METHOD OF MANUFACTURE

#### BACKGROUND OF THE INVENTION

##### 1. Field of the Invention

The present invention relates to a micro-fastening system and, more particularly, to a mechanical micro-fastening system employing a plurality of mating nanoscale fastening elements and a method of manufacturing the same.

##### 2. Description of the Prior Art

Micro-fastening systems per se are utilized to connect distinct components brought into relative contact by strong bonds which span a gap at the interface and generally are less than one micrometer in size. In their most common embodiments, such microfastening systems have generally been in the form of chemical bonds such as adhesive bonds, welds and coatings. Numerous potential disadvantages associated with employing adhesives and coatings are known such as the irreversible nature of the bonds and the potential for degradation at relatively high temperatures. Further, adhesives and coatings generally require smooth dry interfaces which are free of impurities to effectuate high quality bonds. Welding results in a physical deformation of the surfaces being welded; it cannot be used effectively for interconnecting microscopically small components or large interface areas. Thus, there is a need for the mechanical "micro-fastening" system of the present invention.

#### SUMMARY OF THE INVENTION

The micro-fastening system of the present invention employs a plurality of mating nanoscale fastening elements which are obtained by structurally modifying, i.e., functionalizing nanotubes generally and carbon nanotubes particularly. Carbon nanotubes per se consist of a graphite monolayer having the overall shape of a cylinder including an ordered array of hexagonal carbon rings disposed along the cylindrical side walls which may be single or

multi-walled as reported in *Nature*, Vol. 354 (1991) pp. 56 - 58 and *ibid.* Vol. 363 (1993) pp. 603 - 605. The ends of the tubes are often closed by pairs of pentagonal carbon rings. Carbon nanotubes generally range in diameter from one to about 50 nanometers, and may be as long as approximately 0.1 millimeters. While related to carbon fibers, nanotubes are free of atomic scale defects, which accounts for their high tensile strength, as compared to that of the strength of individual graphite layers. Like graphite, carbon nanotubes exhibit  $sp^2$  bonding which gives rise to a relatively high degree of flexibility and resilience. Further, carbon nanotubes are structurally stable nearly up to the melting point of graphite, i.e., up to about 3,500 degrees Celsius.

By functionalizing the carbon nanotubes as will be described in greater detail below, the cylindrical shape can be modified to include bent portions. While it has been suggested generally that carbon nanotubes can be readily functionalized, it has yet to be reported that carbon nanotubes can be specifically functionalized so as to obtain mating fastening elements as herein described.

Among the various applications for the micro-fastening system of the present invention are the assembly of nano-robots useful for micro-surgical procedures, surface coatings, and attachment of metal contacts to integrated semiconductor devices, by way of non-limiting example.

The strength of micro-fastening systems described herein relies on the enormous stability of nanotubes, i.e., their large structural rigidity, the high strength of the bonds anchoring tubes in a substrate and a large number of connections possible on a limited surface area. In contrast to purely mechanical fasteners (such as bolts and screws) which weaken the surfaces to be connected, there is no apparent degradation of the opposing surfaces to be joined under the present invention. Adhesives are typically weaker than most mechanical fasteners and their strength is strongly diminished at higher temperatures. Welding is not practicable for large interfaces, whereas the fastening system of the present invention may be employed for both large and microscopically small interfaces. Bonding technologies excepting the

micro-fastening system of the present invention leave macroscopically large gaps at the interface. Unlike known bonds between substrates, the micro-fastening system of the present invention has an effective thickness of the gap at interface as small as a few nanometers.

5 A further advantage of the present invention is that the surface bonds based on the nanotube based micro-fastening system, while extremely strong, may be re-opened and re-closed, i.e., they are reusable, whereas the surface bonds generated by gluing or welding are permanent. Thus, the micro-fastening system of the present invention is selectively reversible which is  
10 considered to be highly desirable, particularly for self-repair. This reusability or self-repairability is of particular advantage for interconnects exposed to changing forces or changing environmental variables (such as temperature) that result in a different expansion of the individual components brought into relative contact.

15 Still another advantage offered by the micro-fastening system of the present invention is that the conductivity of the fastening elements connecting the corresponding substrates may be varied from metallic to insulating, depending largely on the chemical composition, the diameter and chirality of the nanotubes.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

20 Figures 1(a-c) are a series of views demonstrating the representative closure mechanism and forces for a generic micro-fastening system in accordance with the teachings of the present invention.

25 Figures 1(d-f) are a series of views demonstrating the representative opening mechanism and forces for a micro-fastening system in accordance with the teachings of the present invention.

30 Figure 2 is a schematic view illustrating a way to define the figure of merit of the micro-fastening system wherein the horizontal axis X represents the separation between the surfaces.

Figures 3(a-d) are a series of views demonstrating the representative opening and closure mechanisms and forces for a particular micro-fastening

system based on nanotubes functionalized to form a mating hook and loop arrangement in accordance with the teachings of the present invention.

Figures 4(a-b) are illustrative of alternative mating nanoscale micro-fastening system elements in accordance with the teachings of the present invention.

### **DETAILED DESCRIPTION OF THE INVENTION**

The micro-fastening system 10 of the present invention comprises a plurality of mating nanoscale fastening elements 12 and 12' manufactured by modifying, i.e., functionalizing nanotubes which are generally linear in nature prior to functionalizing. Upon functionalizing the nanotubes 14, fastening elements are obtained in a variety of non-linear forms such as hooks 16 and loops 18 as illustrated in Figs. 3(a-d) and spirals 20 as illustrated in Fig. 4(b) by way of non-limiting example. The nanotubes employed may be composed of carbon, nitrogen, boron or other elements which give rise to layered honeycomb lattice structures. It is important from the outset to note that the nanotubes employed in accordance with the teachings of the present invention may be single walled, multi-walled or at least partially multi-walled over the length of the nanotube. For simplicity, the present invention will hereinafter generally be described in terms of functionalizing graphitic carbon nanotubes.

By "functionalizing" graphitic carbon nanotubes, it is meant that a specific number of pentagons and heptagons are substituted for hexagons within the nanotube or are added along the open edge(s) of the core nanotube which consists of an ordered array of hexagons.

Upon introducing pentagons and heptagons in a predetermined order, the carbon nanotubes will exhibit a locally positive or negative Gaussian curvature that results in a "bend" in the nanotube. By continuing to add pentagons and hexagons in a specific manner, the bend of the nanotube can be grown until the desired shape is obtained.

Upon growing the carbon nanotube to the desired length and shape, a first end 22 of the nanotube 14 may be capped or terminated, e.g., by

introducing or forming a fullerene half dome along the end to be terminated. By providing a fullerene half-dome along an open end of the carbon nanotube, the end of the formed fastening element 12 becomes substantially inert, i.e., non-bonding to other atoms or molecules.

5 A second end 24 of the fastening element which is open, i.e., non-terminated, is bonded to a substrate 26 which may be in the form of various materials including metals, carbon (graphite or diamond), silicon, germanium, polymers and composites of the foregoing, to name a few. Other materials, provided they are capable of attaining a molten state, can also be employed.

10 Since the open end 24 of the nanotube is highly reactive and thus has a natural affinity for bonding to the desired substrate, the fastening element readily attaches to the substrate in a manner whereby the element stands up along the attachment surface. Nanotubes may be assisted in their alignment perpendicular to the surface by applying a strong electric field in that direction. This so-called affinity to migrate toward the surface is at least  
15 partially due to the low surface tension of the nanotube material. As will be understood by those skilled in the art, the tendency for the fastening elements to stand up promulgates mating between corresponding fastening elements.

Carbon nanotubes having ordered pairs of pentagons and heptagons  
20 may occur spontaneously to a limited extent during synthesis, thus forming hook shaped nanotubes as reported in MRS Bulletin, Vol. 19, No. 11, pp 43 - 49 (1994). However, in order to design carbon nanotubes such that they can be used effectively in micro-fastening systems, atomically dispersed catalysts may be necessary. For example, transition metals such as Fe and, more  
25 preferably, Ni, Co and Y have been shown to promote formation of single wall nanotubes or spiral structures as reported in Science 265, 635 (1994).

Curvature of the ends or other portions of relatively straight carbon nanotubes can be also accomplished by employing a template in proximity to a growing nanotube. In this regard, both on energetic and entropic  
30 grounds, a horizontally growing nanotube, when approaching a vertically positioned nanotube used as a template, has a higher probability to form ordered pairs of  $C_5$  and  $C_7$  carbon rings, i.e., pentagons and heptagons which

would cause the former to "wrap around" the latter. As such, specifically functionalized carbon nanotubes 14 useful as fastening elements 12 such as those illustrated in Figs. 4(a-b) can also be prepared without employing catalysts.

As shown in Figs. 1(a-c), only a moderate force  $F_c$  is required to selectively deform the nanotube and thereby accomplish an interconnection between the first and second fastening elements 12 and 12'. A much larger force  $F_o$  is required to break the interconnection between the fastening elements 12 and 12' of components in contact as demonstrated in Figs. 1(d-f). The hatched area in Fig. 2 represents the work required to close and re-open the gap and indicates the efficiency of a particular pair of mating nanoscale fastening elements.

As noted, while the fastening elements 12 and 12' can be formed into a number of different configurations, certain configurations are considered to be preferred. For a generic mechanical micro-fastening system, the opening and closing mechanism is shown in Figs. 1(a-f). Generic fastening elements, shown in these figures, contain a substantially triangular shaped head 30. Under this schematic embodiment the angled surfaces 32 and 32' slide past the other as the fastening elements come into contact as they advance toward an interlocked position. This angular orientation of approximately  $45^\circ$  along surfaces 32 and 32' allows for a minimal amount of lateral deflection of the fastening elements during the attachment step. The attachment surfaces 34 and 34' preferably slope downwardly and away from their respective stems 36 and 36' to form an interconnection requiring a relatively high separation force, i.e.,  $|F_o| > |F_c|$ .

Figs. 3(a-d) show one particular embodiment of the micro-fastening system, consisting of hook 16 and loop 18 fastening elements. Under this embodiment, as the hook and loop elements are advanced toward each other, the first end 22 of the hook deflects until there is sufficient clearance to insert into the aperture 40 of the loop element. As with the embodiment illustrated in Figs. 1(a-f), the hook and loop fastening system requires a



relatively high separation force  $|F_o| > |F_c|$  to detach the fastening elements as compared to the attachment forces.

5 Still other embodiments such as hook 16 to hook 16' fastening as illustrated with reference to Fig. 4a and spiral 20 to hook 16 fastening as illustrated in Fig. 4b are considered as practical applications. In essence, the shape of the resulting fastening elements is a function of the processing parameters, as such various fastening element configurations are contemplated.

10 Additionally, it should be understood that micro-fastening elements having different shapes can be formed upon the same substrate. Thus, alternating rows of specifically shaped fastening elements along a useful substrate is an effective application. Of course, microfastening elements of differing configurations can be randomly applied to a substrate, if desired.

15 While it will be apparent that the preferred embodiments of the invention disclosed are well calculated to fulfill the objects stated, it will be appreciated that the invention is susceptible to modification, variation and change without departing from the spirit thereof.

**CLAIMS**

1. A microfastening system comprising:  
a first fastening element including a plurality of extending  
nanotubes; and  
5 a second fastening element including a plurality of extending  
nanotubes;  
whereby upon joining said first and second fastening elements,  
the extending nanotubes from each element become mechanically  
interconnected.  
10
2. The microfastening system of Claim 1 wherein said at least one  
of first and second fastening elements further comprise a substrate from  
which said nanotubes extend.
- 15 3. The microfastening system of Claim 2 wherein said substrate is  
formed from materials selected from the group consisting of metals, carbon,  
silicon, germanium, polymers and composites thereof.
- 20 4. The microfastening system of Claim 1 wherein said nanotubes  
are at least partially multi-walled.
5. The microfastening system of Claim 1 wherein the nanotubes  
are functionalized to a non-linear shape.
- 25 6. The microfastening system of Claim 5 wherein the non-linear  
nanotubes of said fastening element are selected from hooks, loops, spirals  
and combinations thereof.
- 30 7. The microfastening system of Claim 1 wherein said nanotubes  
of at least one of said fastening elements are selectively deformable.

8. The microfastening system of Claim 1 wherein said fastening elements are reusable.

5 9. A microfastener comprising:  
a substrate including an attachment surface; and  
a plurality of functionalized non-linear nanotubes attached to and  
extending from said attachment surface.

10 10. The microfastener of Claim 9 wherein said substrate is formed  
from materials selected from the group consisting of metals, carbon, silicon,  
germanium, polymers and composites thereof.

15 11. The microfastener of Claim 9 wherein said nanotubes are at  
least partially multi-walled.

12. The microfastener of Claim 9 wherein the non-linear nanotubes  
of said fastening element are selected from hooks, loops, spirals and  
combinations thereof.

20 13. The microfastener of Claim 9 wherein at least some of the  
nanotubes of said microfastener are selectively deformable.

14. A method of manufacturing a microfastener comprising the steps  
of:

25 a) providing a substrate having an attachment surface;  
b) introducing a plurality of open ended nanotubes to said  
substrate whereby said nanotubes are attracted to said attachment surface  
and become affixed thereto.

30 15. The method of Claim 14 wherein said nanotubes are  
functionalized prior to attaching to said substrate.

16. The method of Claim 14 wherein said nanotubes are functionalized during attachment to said substrate.

17. The method of Claim 14 wherein said nanotubes are functionalized after attachment to said substrate.

18. The method of Claim 14 wherein said substrate is formed from materials selected from the group consisting of metals, carbon, silicon, germanium, polymers and composites thereof.

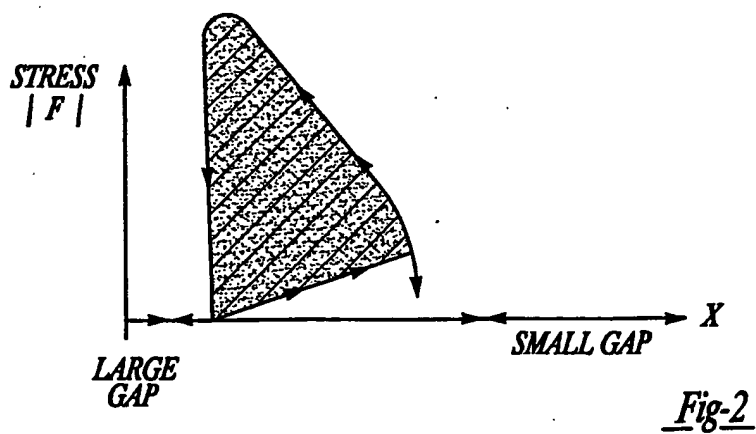
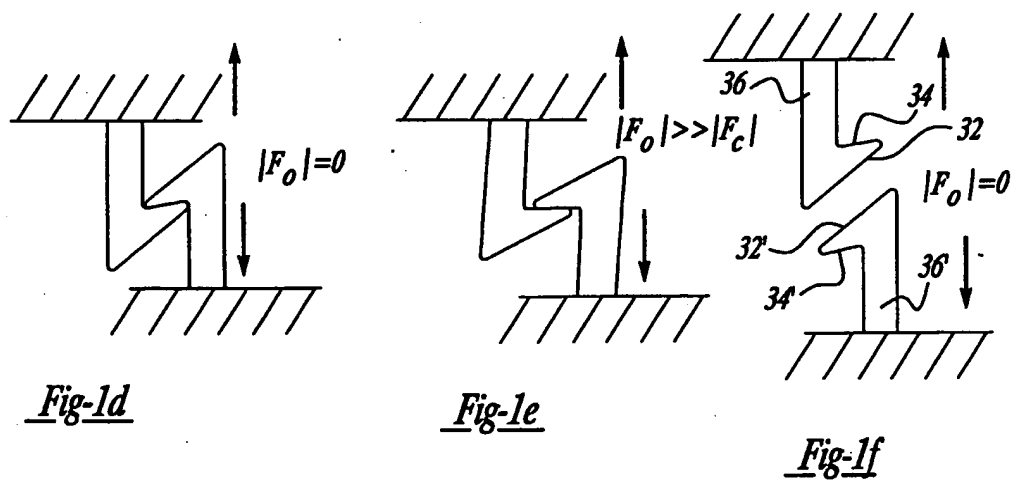
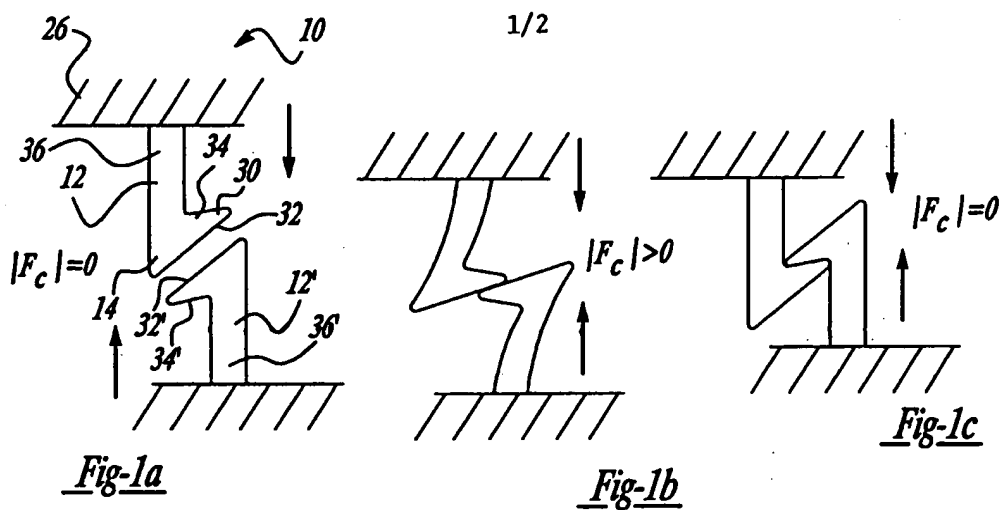
19. The method of Claim 14 wherein said nanotubes are at least partially multi-walled.

20. The method of Claim 14 wherein the non-linear nanotubes of said fastening element are selected from hooks, loops, spirals and combinations thereof.

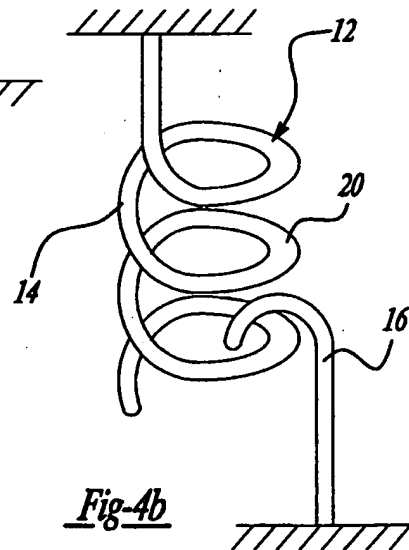
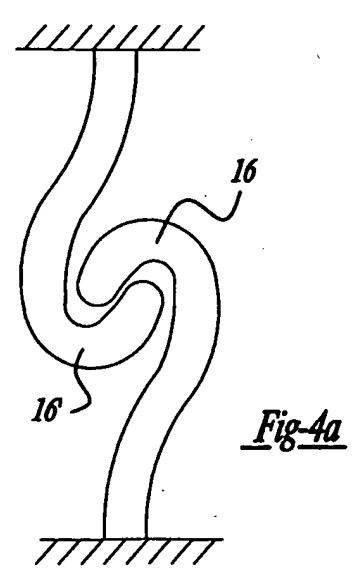
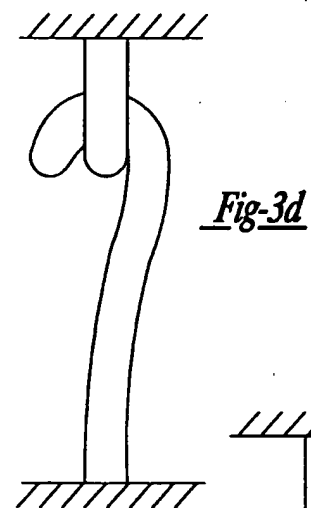
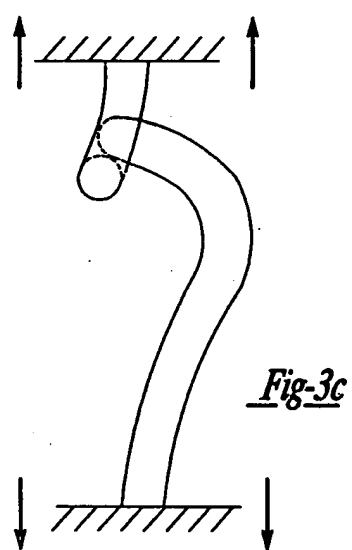
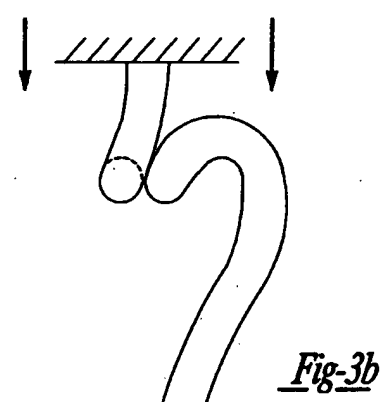
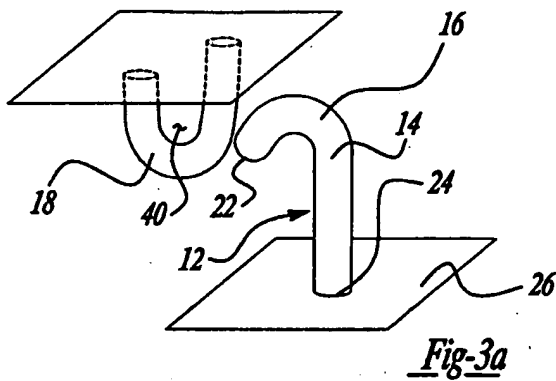
21. The method of Claim 14 wherein at least some of said nanotubes are selectively deformable.

22. The method of Claim 14 wherein said nanotubes are attached to said substrate in the presence of an electric field.

23. The method of Claim 14 wherein said microfastener is reusable.



2/2



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/02897

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(6) :A44B 18/00 US CL :24/442 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : 24/442, 444, 446-452; 423/447.1; 428/420, 100 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DIALOG OneSearch, Chinese Patents ABS 04/1985-02/1999, JAPIO 10/1976-11/1998, DERWENT WPI 1963-1999, US Pat. Full 1990-1999 search terms: nanotube, microfastener, Velcro		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — A	US, 5,464,987 A (IHARA et al.) 07 November 1995 (07/11/95), see the key structure of figure 10.	1-6, 9-12, 14, 15 and 18-20  7, 8, 13, 16, 17 and 21-23
A	US 5,657,516 A (BERG et al.) 19 August 1997 (19/08/97), see the hollow elements of figure 6.	1
A	US 3,921,258 A (BRUMLIK) 25 November 1975 (25/11/75), see the tubular gripping member 10, col. 3, lines 12-14	1
A	US 3,889,322 A (BRUMLIK) 17 June 1975 (17/06/75), see figures 12g and 12h.	1
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "B" earlier document published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "A" document member of the same patent family	
Date of the actual completion of the international search 01 JUNE 1999		Date of mailing of the international search report 17 JUN 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer <i>James R. Brittain</i> JAMES R. BRITTAIN Telephone No. (703) 308-2168

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/US99/02897

**C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,531,733 A (HALL) 30 June 1985 (30/06/85), see the hollow prongs 206, col. 6, lines 63-64.	1